

Flat bands in Weaire-Thorpe model and silicene

Y. Hatsugai

Division of Physics and Tsukuba Research Center for Interdisciplinary Materials
Science, University of Tsukuba, Ibaraki 305-8571, Japan
Center for Innovative Integrated Electronic Systems, Tohoku University, Sendai,
Miyagi 980-0845, Japan

E-mail: hatsugai@rhodia.ph.tsukuba.ac.jp

K. Shiraishi

Department of Computational Science and Engineering, Nagoya University, Nagoya
464-8603, Japan
Center for Innovative Integrated Electronic Systems, Tohoku University, Sendai,
Miyagi 980-0845, Japan

H. Aoki

Department of Physics, University of Tokyo, Tokyo 113-0033 Japan

Abstract. In order to analytically capture and identify peculiarities in the electronic structure of silicene, Weaire-Thorpe(WT) model, a standard model for treating three-dimensional (3D) silicon, is applied to silicene with the buckled 2D structure. In the original WT model for four hybridized sp^3 orbitals on each atom along with inter-atom hopping, the band structure can be systematically examined in 3D, where flat (dispersionless) bands exist as well. For examining silicene, here we re-formulate the WT model in terms of the overlapping molecular-orbital (MO) method which enables us to describe flat bands away from the electron-hole symmetric point. The overlapping MO formalism indeed enables us to reveal an important difference: while in 3D the dispersive bands with cones are sandwiched by doubly-degenerate flat bands, in 2D the dispersive bands with cones are sandwiched by triply-degenerate and non-degenerate (nearly) flat bands, which is consistent with the original band calculation by Takeda and Shiraishi. Thus emerges a picture for why the whole band structure of silicene comprises a pair of dispersive bands with Dirac cones with each of the band touching a nearly flat (narrow) band at Γ . We can also recognize that, for band engineering, the bonds perpendicular to the atomic plane are crucial, and that a ferromagnetism or structural instabilities are expected if we can shift the chemical potential close to the flat bands.

1. Introduction

After the physics of graphene was kicked off, originally by a theoretical prediction for a massless Dirac fermion by Wallace[1] back in the 1950's and by a recent experimental realization[2], interests are extended to wider class of systems. Unusual behaviours of the massless Dirac fermions are then experimentally confirmed and theoretically analysed[3]. History seems to repeat itself, for silicene: the material was theoretically predicted in the early 1990's by one of the present authors and Takeda[4], and the material began to be synthesised recently[5, 6, 7], after such a long latent period. Successful synthesis of silicene on Ag has triggered intense attentions in both physics and material science. In graphene, the carriers, being in a atomically flat system, are π -electrons arising from the sp^2 hybridization of carbon orbitals. In silicene, by contrast, the honeycomb lattice is buckled, so that a sp^3 character of Si is involved, which is crucial as pointed out already in [4]. Thus silicene is not just a Si analogue of graphene, but distinct multi-orbital characters should appear in its electronic structure.

Hence silicene has a larger degree of freedom than graphene as a target material for applications and also theoretical considerations. In the present paper, we focus on this multi-orbital feature of silicene, where we opt for a simplified model, namely we propose to introduce as an extension of the Weaire-Thorpe(WT) model, which was originally conceived for a three-dimensional (3D) silicon with sp^3 orbits in a tight-binding model on a diamond lattice[8]. In the original WT model for four sp^3 orbitals on each atom along with inter-atom hopping in 3D, the band structure is systematically examined, and two singular dispersions arise: One is a massless Dirac cone, and the other is dispersionless (flat) band[9]. Massless Dirac cones in three dimensions are topologically protected. In two dimensions, they can arise, with supplemental symmetry protections, as in graphene and silicene.[10]. On the other hand, the flat bands are not protected by symmetry in realistic materials. Still, however, the flat bands can have some topological/geometrical origins reflecting the multi-orbital character of a given material as we describe in the present paper. For silicene, here we re-formulate the WT model in terms of the overlapping molecular-orbital (MO) method[11] discussed by Hatsugai and Maruyama, which contains WT and enables us to describe flat bands away from the electron-hole symmetric point. The overlapping MO formulation indeed enables us to pin point, algebraically, an important difference: while in 3D the dispersive bands with cones are sandwiched by doubly-degenerate flat bands, in 2D the dispersive bands with cones are sandwiched by triply-degenerate and non-degenerate (nearly) flat bands, which is consistent with the original band calculation by Takeda and Shiraishi[4]. Thus emerges a picture for why the whole band structure of silicene comprises dispersive bands with Dirac cones along with nearly flat (narrow) bands.

In the present paper, we first start with an *overlapping molecular orbital theory*[11]. Applying this to the WT model enables us to generically treat the flat bands away from the electron-hole symmetric point in multi-orbital models while the usual flat-band theories[12, 13, 14, 15] focus on those at the electron-hole symmetric point. We

then gives a picture for silicene in this formalism, and compare the result with the band structure due to Takeda and Shiraishi. We finally discuss that the nearly flat bands imply large density of states (DOS), which will give an interesting possibility for inducing instabilities into symmetry-broken states such as ferromagnetism or structural changes. For the band engineering the bonds perpendicular to the atomic plane are suggested to be crucial.

2. Overlapping molecular orbitals and flat bands

Let us start with describing a class of lattice model Hamiltonians in terms of molecular orbitals proposed by Hatsugai and Maruyama[11], which is here explained to make the present paper self-contained. Consider fermions on an N -site lattice with the creation operator, c_i^\dagger , for the sites $i = 1, \dots, N$ with $\{c_i^\dagger, c_j\} = \delta_{ij}$. After shifting the origin of energy by μ , let us consider the case in which the Hamiltonian is given as a sum of *overlapping molecular orbitals* $m(= 1, \dots, M)$ as

$$H - \mu\mathcal{N} = \sum_{m=1}^M \mathcal{E}_m C_m^\dagger C_m,$$

where $\mathcal{N} = \sum_{i=1}^N c_i^\dagger c_i$ is the number operator of the fermions. The coefficient $\mathcal{E}_m \in \mathbb{R}$ is the energy level of the molecular orbital m , while C_m^\dagger creates the molecular orbital as

$$C_m^\dagger = \sum_{i=1}^N c_i^\dagger \psi_{i,m} = c^\dagger \psi_m, \quad c^\dagger = (c_1^\dagger, \dots, c_N^\dagger), \quad \psi_m = \begin{bmatrix} \psi_{1,m} \\ \vdots \\ \psi_{N,m} \end{bmatrix},$$

where ψ_m is the wavefunction of the molecular orbital m . We do *not* require translational symmetry in the system or in the molecular orbitals as is the case with the WT model.

Then we have a simple theorem that $H - \mu\mathcal{N}$ has $(N - M)$ -fold degenerate zero-energy states when $N - M > 0$, where M is the total number of the molecular orbitals in the whole real space. The number of the zero energy states $N - M$ can be macroscopic. Since the theorem is general, we can apply it to random systems but to periodic systems as well. Then we can characterise the wavefunctions as Bloch states, and N may be regarded as the number of energy bands when we express the Hamiltonian in the Bloch basis. The total number of the molecular orbitals, M , in this Bloch basis corresponds to the total number of the terms in the Hamiltonian in the momentum representation, which varies from a model to another, as we shall see.

Note here that if there are zero-energy states in the present Hamiltonian, they should be located at $E = \mu$ for the original Hamiltonian H . Thus we can describe non-zero energy states algebraically by suitably choosing μ . This is trivial but useful as we demonstrate in Secs.3 and 4.

While we can normalize the molecular orbitals as $\psi^\dagger \psi = 1$, they overlap with each other in general, which implies the anticommutation relation $\{C_m, C_{m'}^\dagger\}$ may not be

simple. We further decompose the Hamiltonian as

$$H - \mu\mathcal{N} = \mathbf{c}^\dagger h \mathbf{c}, \quad h = \sum_{m=1}^M \mathcal{E}_m P_m,$$

where $P_m = \psi_m \psi_m^\dagger$ is a projection operator with $P_m^2 = P_m$. For non-orthogonal MO's we have $P_m P_{m'} \neq 0$ when the different MO's m and m' have a non zero overlap. Since P_m 's span a one-dimensional space, the dimension of the Hamiltonian h is at most M . We still express the Hamiltonian as an $N \times N$ matrix, this should be redundant, namely the $(N-M)$ -dimensional subspace has to be null, with h having $N-M$ zero eigenvalues. We can explicitly show this by writing the $N \times N$ matrix h as (see footnote 4 of the Ref.[11])

$$\boxed{h} = \boxed{\Psi} \boxed{\mathcal{E}} \boxed{\Psi^\dagger}, \quad \boxed{\Psi} = \begin{array}{|c|} \hline \psi_1 \\ \hline \end{array} \cdots \begin{array}{|c|} \hline \psi_M \\ \hline \end{array}$$

where $\mathcal{E} = \text{diag}(\mathcal{E}_1, \dots, \mathcal{E}_M)$ is an M -dimensional diagonal matrix and Ψ is an $N \times M$ matrix composed of the molecular orbitals (ψ 's) as columns. Then, by a simple algebra, the secular equation for h becomes

$$\det_N(\lambda E_N - h) = \lambda^N \det_N(E_N - \lambda^{-1} \Psi \mathcal{E} \Psi^\dagger) = \lambda^{N-M} \det_M(\lambda E_M - \mathcal{E} \Psi^\dagger \Psi) = 0,$$

where E_n is an n -dimensional unit matrix. Then one can see that h has $(N-M)$ -fold degenerate zero eigenvalues $\lambda = 0$. These zero-energy states are topological in that they are stable against continuous deformations of the parameters such as \mathcal{E}_m 's and ψ_{im} 's. These zero states are stable as far as the number of the molecular orbitals is fixed. It is a finite dimensional analogue of the Atiyah-Singer's index theorem[12].

Following the idea, we state the theorem in a slightly extended form, which we shall use later in the present paper. For the projection $P_m = P_m^2 = P_m^\dagger$, let us define its dimension, $\dim P_m = \text{Tr} P_m = \text{rank } P_m$. Since the projection operator has eigenvalues 0 or 1, the dimension is a number of nonzero eigenvalues of P_m , which also coincides with the rank of the matrix representation of P_m . Then the number of zero modes, Z , should satisfy a condition,

$$Z \geq N - \sum_m \dim P_m.$$

We note here that the flat bands at the zero energy of the chiral symmetric models[12, 9, 13, 14, 15] have been discussed with the argument presented above, where a square of the Hamiltonian is considered. Since the hamiltonian in the chiral class is written as $\begin{bmatrix} O & D \\ D^\dagger & O \end{bmatrix}$ in a suitable basis, its square is $\begin{bmatrix} DD^\dagger & O \\ O & D^\dagger D \end{bmatrix}$. When D is an $N \times M$ matrix ($N > M$), one may identify $\Psi = D$ and $\mathcal{E} = E_M$. The $(1, 1)$ block of this squared Hamiltonian, DD^\dagger , corresponds to the present hamiltonian. Then the theorem here guarantees the existence of zero-energy states of the chiral symmetric Hamiltonian

with degeneracy $N - M$. We can also note that the overlapping molecular orbitals in real space are discussed in the context of the rigorous treatment of the ferromagnetism on the Hubbard model[13, 16, 17]. Non particle-hole symmetric flat bands on special shape of the lattice (partial line graphs) are discussed as well[18]. Then the relation to the present analysis can be an interesting problem, and should be discussed in the future.

3. Weaire-Thorpe model

Weaire and Thorpe considered a simple but multi-orbital tight-binding model for the sp^3 electrons on the diamond lattice[8], where the original motivation was to treat amorphous silicone. Let us reproduce the model here for later references. We start with sp^3 -hybridized orbitals on a single tetrahedron. The local Hamiltonian for the tetrahedron reads

$$H_{sp^3} = \epsilon_s c_s^\dagger c_s + \epsilon_p (c_{p_x}^\dagger c_{p_x} + c_{p_y}^\dagger c_{p_y} + c_{p_z}^\dagger c_{p_z}) \equiv \mathbf{c}^\dagger h_{sp^3} \mathbf{c},$$

where c_i ($i = s, p_x, p_y, p_z$) is an annihilation operator of the bond orbitals with energy levels ϵ_s for the s orbital and ϵ_p for the p orbitals, and

$$h_{sp^3} = \epsilon_p E_4 + V_1 \begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \end{bmatrix}, \quad \mathbf{c} = \begin{bmatrix} c_0 \\ c_1 \\ c_2 \\ c_3 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 \end{bmatrix} \begin{bmatrix} c_s \\ c_{p_x} \\ c_{p_y} \\ c_{p_z} \end{bmatrix}.$$

Here E_4 is the 4×4 unit matrix, and $V_1 = \frac{1}{4}(\epsilon_s - \epsilon_p)$ is proportional to the s-p level offset. With this bond basis, the WT model for the silicon atoms on the diamond lattice considers only the hopping, denoted by V_2 , between the bond-sharing orbitals.

For the diamond lattice (See Fig.1(a)), the Hamiltonian in the Bloch picture of the WT model (H_k in the appendix B of [8], but note that here we take the origin of energy at ϵ_p , so that the energy in [8] is shifted by $-V_1$ from ours) is written as

$$H_{WT}(\mathbf{k}) = \begin{bmatrix} V_1 & V_1 & V_1 & V_1 & V_2 & 0 & 0 & 0 \\ V_1 & V_1 & V_1 & V_1 & 0 & V_2 & 0 & 0 \\ V_1 & V_1 & V_1 & V_1 & 0 & 0 & V_2 & 0 \\ V_1 & V_1 & V_1 & V_1 & 0 & 0 & 0 & V_2 \\ V_2 & 0 & 0 & 0 & V_1 & V_1 e^{i(k_y + k_z)} & V_1 e^{i(k_z + k_x)} & V_1 e^{i(k_x + k_y)} \\ 0 & V_2 & 0 & 0 & V_1 e^{-i(k_y + k_z)} & V_1 & V_1 e^{i(k_x - k_y)} & V_1 e^{-i(k_z - k_x)} \\ 0 & 0 & V_2 & 0 & V_1 e^{-i(k_z + k_x)} & V_1 e^{-i(k_x - k_y)} & V_1 & V_1 e^{i(k_y - k_z)} \\ 0 & 0 & 0 & V_2 & V_1 e^{-i(k_x + k_y)} & V_1 e^{i(k_z - k_x)} & V_1 e^{-i(k_y - k_z)} & V_1 \end{bmatrix}$$

$$= \begin{bmatrix} H_V(0) & V_2 E_4 \\ V_2 E_4 & H_V(\mathbf{k}) \end{bmatrix},$$

$$H_V(\mathbf{k}) = 4V_1 \psi_{\mathbf{k}} \psi_{\mathbf{k}}^\dagger,$$

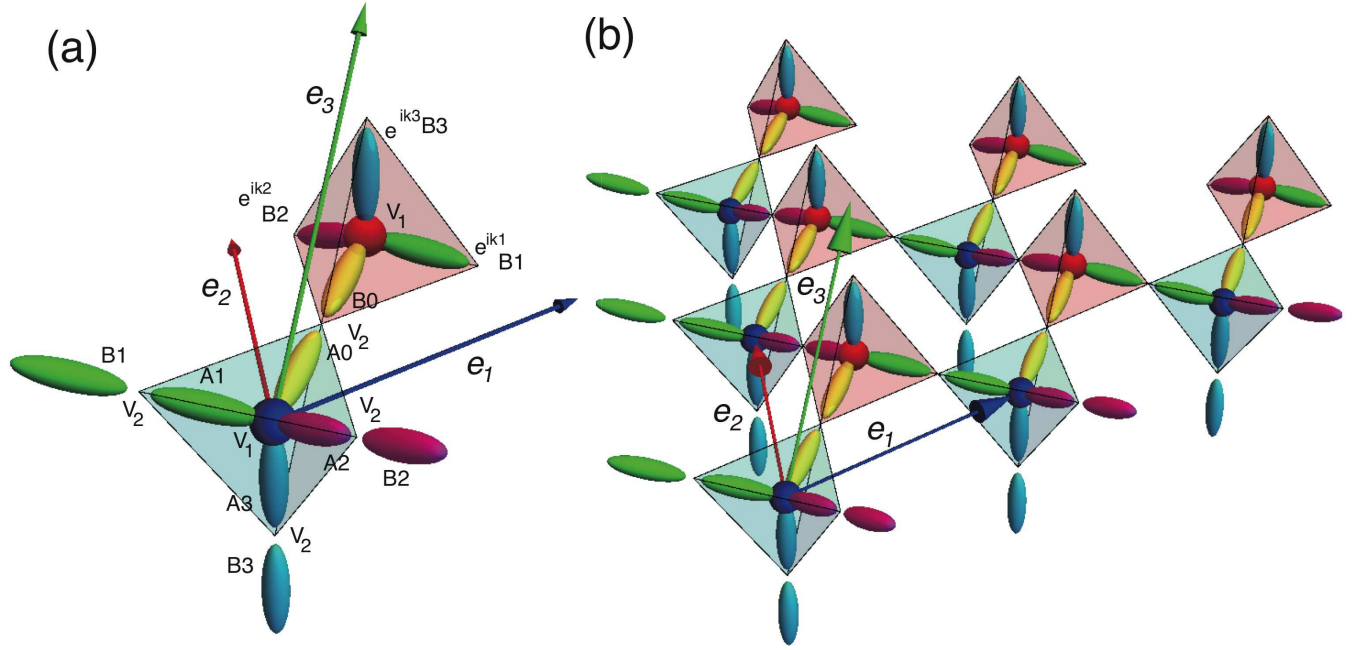


Figure 1. (a): Unit cell of the WT model for the diamond lattice. (b) Array of the tetrahedra for the two-dimensional atomic layer (silicene), which has two primitive vectors e_1, e_2 . If we stack the layer with a primitive vector e_3 , the WT model in 3D is recovered.

$$\psi_{\mathbf{k}} = \frac{1}{2} \begin{bmatrix} e^{i(k_x+k_y+k_z)} \\ e^{ik_x} \\ e^{ik_y} \\ e^{ik_z} \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 1 \\ e^{-ik_1} \\ e^{-ik_2} \\ e^{-ik_3} \end{bmatrix} e^{i(k_x+k_y+k_z)},$$

where $k_1 = k_y + k_z$, $k_2 = k_z + k_x$, $k_3 = k_x + k_y$, and $\psi_{\mathbf{k}}\psi_{\mathbf{k}}^\dagger \propto H_V$ is a projection onto the space spanned by $\psi_{\mathbf{k}}$. We can then apply the discussion in sec.2 to note that 4×4 matrix $H_V(\mathbf{k})$ has at most one nonzero energy that corresponds to a localised molecular orbital at each tetrahedron, while there are three zero-energy flat bands (in the present choice of the origin of energy).

With this observation, we can introduce two representations for the 8×8 Hamiltonian as $H_{WT}(\mathbf{k}) \pm V_2 E_8$, where E_8 is an 8×8 unit matrix. Although one might think the choice of the origin of the energy to be irrelevant, the whole point here is: we want to deal with flat bands that have nonzero energies. To do that, we can shift the origin of the energy to apply an algebraic argument. Now, if we take the plus sign, we have

$$\begin{aligned} H_{WT}(\mathbf{k}) + V_2 E_8 &= \begin{bmatrix} H_V(0) & 0 \\ 0 & H_V(\mathbf{k}) \end{bmatrix} + V_2 \begin{bmatrix} E_4 & E_4 \\ E_4 & E_4 \end{bmatrix} \\ &= 4V_1 P_1 + 4V_1 P_2 + 2V_2 P_{3+}, \end{aligned}$$

$$P_1 = \begin{bmatrix} \psi_0 \psi_0^\dagger & O \\ O & O \end{bmatrix} = \Psi_1 \Psi_1^\dagger, \quad P_2 = \begin{bmatrix} O & O \\ O & \psi_{\mathbf{k}} \psi_{\mathbf{k}}^\dagger \end{bmatrix} = \Psi_2 \Psi_2^\dagger, \quad P_{3+} = \frac{1}{2} \begin{bmatrix} E_4 & E_4 \\ E_4 & E_4 \end{bmatrix} = \Psi_{3+} \Psi_{3+}^\dagger,$$

$$\Psi_1 = \frac{1}{2} \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \quad \Psi_2 = \frac{1}{2} \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ e^{-ik_1} \\ e^{-ik_2} \\ e^{-ik_3} \end{bmatrix}, \quad \Psi_{3+} = \frac{1}{\sqrt{2}} \begin{bmatrix} E_4 \\ E_4 \end{bmatrix},$$

where P_i 's are projections with $P_i^2 = P_i$ and $\dim P_i = \text{Tr } \Psi_i \Psi_i^\dagger = \text{Tr } \Psi_i^\dagger \Psi_i = 1, 1, 4$ respectively for $i = 1, 2, 3+$, and $\Psi_1^\dagger \Psi_1 = \Psi_2^\dagger \Psi_2 = 1, \Psi_{3+}^\dagger \Psi_{3+} = E_4$. If we count the dimensions, $H_{WT}(\mathbf{k}) + V_2 E_8$ has at most $\dim P_1 + \dim P_2 + \dim P_{3+} = 1 + 1 + 4$ nonzero-energy bands, that is, there are $8 - 6 = 2$ zero-energy flat bands.

Similarly we have

$$H_{WT}(\mathbf{k}) - V_2 E_8 = \begin{bmatrix} H_V(0) & 0 \\ 0 & H_V(\mathbf{k}) \end{bmatrix} - V_2 \begin{bmatrix} E_4 & -E_4 \\ -E_4 & E_4 \end{bmatrix} \\ = 4V_1 P_1 + 4V_1 P_2 - 2V_2 P_{3-},$$

$$P_{3-} = \Psi_{3-} (\Psi_{3-})^\dagger,$$

$$\Psi_{3-} = \frac{1}{\sqrt{2}} \begin{bmatrix} -E_4 \\ E_4 \end{bmatrix},$$

where P_{3-} is a projection similar to P_{3+} . Now we see that $H_{WT} - V_2 E_8$ has at most $1 + 1 + 4$ nonzero-energy bands, that is, there are again two zero-energy flat bands.

Hence we end up with two flat bands at each of $E = \pm V_2$ in the WT Hamiltonian. To compare with Ref.[8], we need to shift the energy, after which the flat bands are at $-V_1 \pm V_2$, since our choice of the H_{WT} is shifted by $-V_1 E_8$ from the hamiltonian in Ref.[8]. An essential point is that we have succeeded in describing the *flat bands at nonzero energies algebraically* in terms of the overlapping molecular orbitals, here exemplified in the WT model.

4. Silicene in a Weaire-Thorpe type model

Now we come to the original aim at describing silicene. We start with an observation that 2D silicene can also be captured in a manner similar to the WT model in 3D. As indicated in Fig.1(b), we have three primitive vectors, e_1, e_2, e_3 , from which we have three reciprocal vectors for the 3D diamond lattice. Corresponding 2D momentum components are given by (k_1, k_2) with $k_3 = 0$. The Hamiltonian can be obtained from

that in 3D by cutting the bonds at the blue bonds in Fig.1. Then the Hamiltonian as a simple extension of the WT model for silicene can be taken as

$$H_{\text{Silicene}}^0 = \begin{bmatrix} H_V(0) & V_2 E_4^C \\ V_2 E_4^C & H_V(\mathbf{k}) \end{bmatrix}, \quad E_4^C = \begin{bmatrix} E_3 & \\ & 0 \end{bmatrix} = E_4 - \mathcal{E}, \quad \mathcal{E} = \text{diag}(0, 0, 0, 1).$$

We have to note that the bonds normal to the two-dimensional plane, which are originally dangling bonds after the dissection but can be treated with hydrogen termination for instance, are different from the other bonds. A simple way for implementing this is to modify the Hamiltonian into

$$H_{\text{Silicene}}^{\epsilon_H}(\mathbf{k}) = \begin{bmatrix} H_V(0) - \epsilon_H \mathcal{E} & V_2 E_4^C \\ V_2 E_4^C & H_V(\mathbf{k}) - \epsilon_H \mathcal{E} \end{bmatrix},$$

where the energy ϵ_H can be controlled by how the bond is chemically terminated.

Now, an interesting observation is that one can precisely apply the discussion given in Sec.2 to show that the model has flat bands. This follows from a simple observation that

$$\begin{aligned} H_{\text{Silicene}}^{\epsilon_H} + V_2 E_8 &= 4V_1 P_1 + 4V_1 P_2 + V_2 \begin{bmatrix} E_4^C & E_4^C \\ E_4^C & E_4^C \end{bmatrix} + (V_2 - \epsilon_H) \begin{bmatrix} \mathcal{E} & O \\ O & \mathcal{E} \end{bmatrix} \\ &= 4V_1 P_1 + 4V_1 P_2 + 2V_2 P_{3+}^C + (V_2 - \epsilon_H) P_5, \\ H_{\text{Silicene}}^{\epsilon_H} - V_2 E_8 &= 4V_1 P_1 + 4V_1 P_2 - V_2 \begin{bmatrix} E_4^C & -E_4^C \\ -E_4^C & E_4^C \end{bmatrix} - (V_2 + \epsilon_H) \begin{bmatrix} \mathcal{E} & O \\ O & \mathcal{E} \end{bmatrix} \\ &= 4V_1 P_1 + 4V_1 P_2 - 2V_2 P_{3-}^C - (V_2 + \epsilon_H) P_5, \end{aligned}$$

where

$$\begin{aligned} P_{3\pm}^C &= \frac{1}{2} \begin{bmatrix} E_4^C & \pm E_4^C \\ \pm E_4^C & E_4^C \end{bmatrix} = \Psi_{3\pm}^C (\Psi_{3\pm}^C)^\dagger, \\ \Psi_{3\pm}^C &= \frac{1}{\sqrt{2}} \begin{bmatrix} \pm E_4^C \\ E_4^C \end{bmatrix}, \\ (\Psi_{3\pm}^C)^\dagger \Psi_{3\pm}^C &= E_4^C = (E_4^C)^2, \quad \text{Tr} E_4^C = 3, \\ P_5 &= \Psi_5 \Psi_5^\dagger = \begin{bmatrix} \mathcal{E} & O \\ O & \mathcal{E} \end{bmatrix} = P_5^2, \\ \Psi_5 &= (\Psi_{5,1}, \Psi_{5,2}), \quad \Psi_{5,1} = \begin{bmatrix} \mathcal{E} \\ O \end{bmatrix}, \quad \Psi_{5,2} = \begin{bmatrix} O \\ \mathcal{E} \end{bmatrix}, \\ \Psi_{5,1} \Psi_{5,1}^\dagger &= \begin{bmatrix} \mathcal{E} & O \\ O & O \end{bmatrix}, \quad \Psi_{5,2} \Psi_{5,2}^\dagger = \begin{bmatrix} O & O \\ O & \mathcal{E} \end{bmatrix}, \\ \Psi_{5,i}^\dagger \Psi_{5,i} &= \mathcal{E}^2 = \mathcal{E}, \quad (i = 1, 2), \quad \Psi_{5,1}^\dagger \Psi_{5,2} = \Psi_{5,2}^\dagger \Psi_{5,1} = O, \\ \Psi_5^\dagger \Psi_5 &= \begin{bmatrix} \Psi_{5,1}^\dagger \Psi_{5,1} & \Psi_{5,1}^\dagger \Psi_{5,2} \\ \Psi_{5,2}^\dagger \Psi_{5,1} & \Psi_{5,2}^\dagger \Psi_{5,2} \end{bmatrix} = \begin{bmatrix} \mathcal{E} & O \\ O & \mathcal{E} \end{bmatrix}. \end{aligned}$$

The dimensions of the projections are evaluated as

$$\begin{aligned}\dim P_{3\pm}^C &= \text{Tr} \Psi_{3\pm}^C \Psi_{3\pm}^{C\dagger} = \text{Tr} \Psi_{3\pm}^{C\dagger} \Psi_{3\pm}^C = \text{Tr} E_4^C = 3, \\ \dim P_5 &= \text{Tr} P_5 = \text{Tr} \Psi_5 \Psi_5^\dagger = \text{Tr} \Psi_5^\dagger \Psi_5 = 2\text{Tr} \mathcal{E} = 2.\end{aligned}$$

Since we have now expressed the Hamiltonian as a linear combination of projection operators, we can see that the wavefunctions associated with P_1 and P_2 are localised within each tetrahedron, the ones with P_5 are localised within the bonds perpendicular to the plane while the ones with $P_{3\pm}^C$ extend over the 2D plane. Then counting the dimensions tells us that $H_{\text{Silicene}}^{\epsilon_H} \pm V_2 E_8$ has at most $\dim P_1 + \dim P_2 + \dim P_{3\pm} + \dim P_5 = 1 + 1 + 3 + 2 = 7$ nonzero-energy bands, that is, there is a $8-7=1$ flat band at $\pm V_2$ generically.

At a special point of $\epsilon_H = \pm V_2$, the coefficient of the projection P_5 for the expansion of $H_{\text{Silicene}}^{\epsilon_H=\pm V_2} \pm V_2 E_8$ happen to vanish. Then additional two dimensional space of the Hamiltonian becomes null, which makes the flat bands at energies $\mp V_2$ three-fold degenerate.

As for the signs of the parameters, one has $V_1 < 0$ since $\epsilon_s < \epsilon_p$, and $V_2 < 0$ since the hopping gains energy. Further it is natural to assume the bonds normal to the plane are close to be a dangling bond, that is $\epsilon_H < 0$ for a free-standing silicene. Then we may consider the case $\epsilon_H = V_2$ belongs to a regime that contains a free-standing silicene. Thus we can see algebraically that the difference in the structure of the Hamiltonian produces the following: while in 3D the dispersive bands with Dirac cones are sandwiched by doubly-degenerate flat bands, the band structure in 2D silicene has dispersive bands with cones sandwiched by triply-degenerate flat bands and a non-degenerate flat band.

Now let us demonstrate the above analytic formulation by numerical results for the band structure in Fig.2. Panel (a) depicts the ideal case of $\epsilon_H = V_2 = -1.0$, where we can indeed see the triply-degenerate flat bands at $E = -V_2 = 1$ along with a non-degenerate flat band at $E = V_2 = -1$. The result confirms the analytic discussion above. Panel (b) depicts a general case of $\epsilon_H < V_2 = -1$, where we can see that the two out of the three flat bands become somewhat dispersive around $E = -\epsilon_H$ while one flat band remains to be flat at $E = -V_2 = 1$. The two nearly-flat bands derive from the dangling bonds perpendicular to the plane. Interestingly, if we compare the result for the dispersion of silicene obtained by Takeda and Shiraishi[4] as reproduced in Fig.3 here, we can see that they roughly agree with each other in terms of the bands' widths, ordering and multiplicity. Specifically, we can make the following observation. In both of the realistic band structure[4] and the present algebraic treatment for silicene, we have basically two bands that contain Dirac dispersions. The bands are sandwiched by two narrow (ideally flat) bands, each of which touches the dispersive ones at Γ point. Above these, there are two nearly-flat bands[4]. Thus the three narrow bands above the Dirac cone can be traced back to the three-fold degenerate flat bands in the idealised model. Of course, this is only a rough mapping, but these qualitative agreements in the band structure between the WT-like model and the realistic band calculation gives an insight

into a physical origin of the electronic band structure of silicene. The existence of the (nearly) flat bands has an intuitive origin as well. If electrons hop as molecular orbitals, this imposes a strong constraint on the description in terms of the original electron. Namely, the degrees of freedom other than the molecular-orbital hopping remain more or less frozen, which form the nearly-flat (or less dispersive) bands.

Within the present simple model, one may expect the electrons at the perpendicular bonds can be stabilized by the hydrogen termination. It can be modeled as $\epsilon_H = -V_2 > 0$. Then the flat bands originally situated at $-V_2 > 0$ will move down to V_2 , that is, below the energy region of the Dirac cones. Then the Fermi energy, which is originally situated at the Dirac point since the sp^3 -bands are half-filled in silicene, will move away from the original Dirac point.

Dirac cones and effects of buckling

We can even extend the present argument when there is some buckling in the structure. For this we start with an observation that existence of the Dirac cones in silicene is due to the time-reversal (T) and crystal symmetry (e.g. reflection, R , that exchanges bonds 1 and 2)[1, 19, 20]. This is readily seen in the present model, where the momentum dependence is expressed in terms of $\psi_{\mathbf{k}}$. At K and K' points, $\psi_{\mathbf{k}}$ is expressed and transformed as

$$\psi_{\mathbf{k}} = \frac{1}{2} \begin{bmatrix} 1 \\ \omega \\ \omega^2 \\ 1 \end{bmatrix}, \quad TR\psi_{\mathbf{k}} = \frac{1}{2}T \begin{bmatrix} 1 \\ \omega^2 \\ \omega \\ 1 \end{bmatrix} = \psi_{\mathbf{k}},$$

with $\omega \neq 1$ being a nontrivial cubic root of unity, which is the origin of the degeneracy at K and K'. Since the degeneracy is lifted at the general momentum, the energy gap is linearly vanishing (Dirac cones) around K and K'. The property is stable as far as the symmetries T and R remain.

Then what are the effects of the buckling in the sp^3 structure observed in silicene? Since the main effect of the buckling is a modification of the bond-to-bond angles among the sp^3 orbitals, the local hamiltonian within a tetrahedron depends on the buckling angle θ as

$$\begin{aligned} h_{\text{local}}(\theta) &= \sum_{\langle i,j \rangle} V_{ij} c_i^\dagger c_j + \text{h.c.}, \\ V_{ij} &= \begin{cases} V_1 & (\langle i,j \rangle = \langle 01 \rangle, \langle 12 \rangle, \langle 20 \rangle) \\ V'_1 & (\langle i,j \rangle = \langle 03 \rangle, \langle 13 \rangle, \langle 23 \rangle) \end{cases} \\ \frac{V'_1}{V_1} &= \frac{\cos \theta}{\cos \theta_0}, \quad \cos \theta_0 = -\frac{1}{3}, \end{aligned}$$

where c_3 is the annihilation operator for the bond that is perpendicular to the silicene plane. Since the two bonds coupling the neighboring tetrahedra remain straight even with the buckling, the inter-site term V_2 is not modified. As far as the buckling is small,

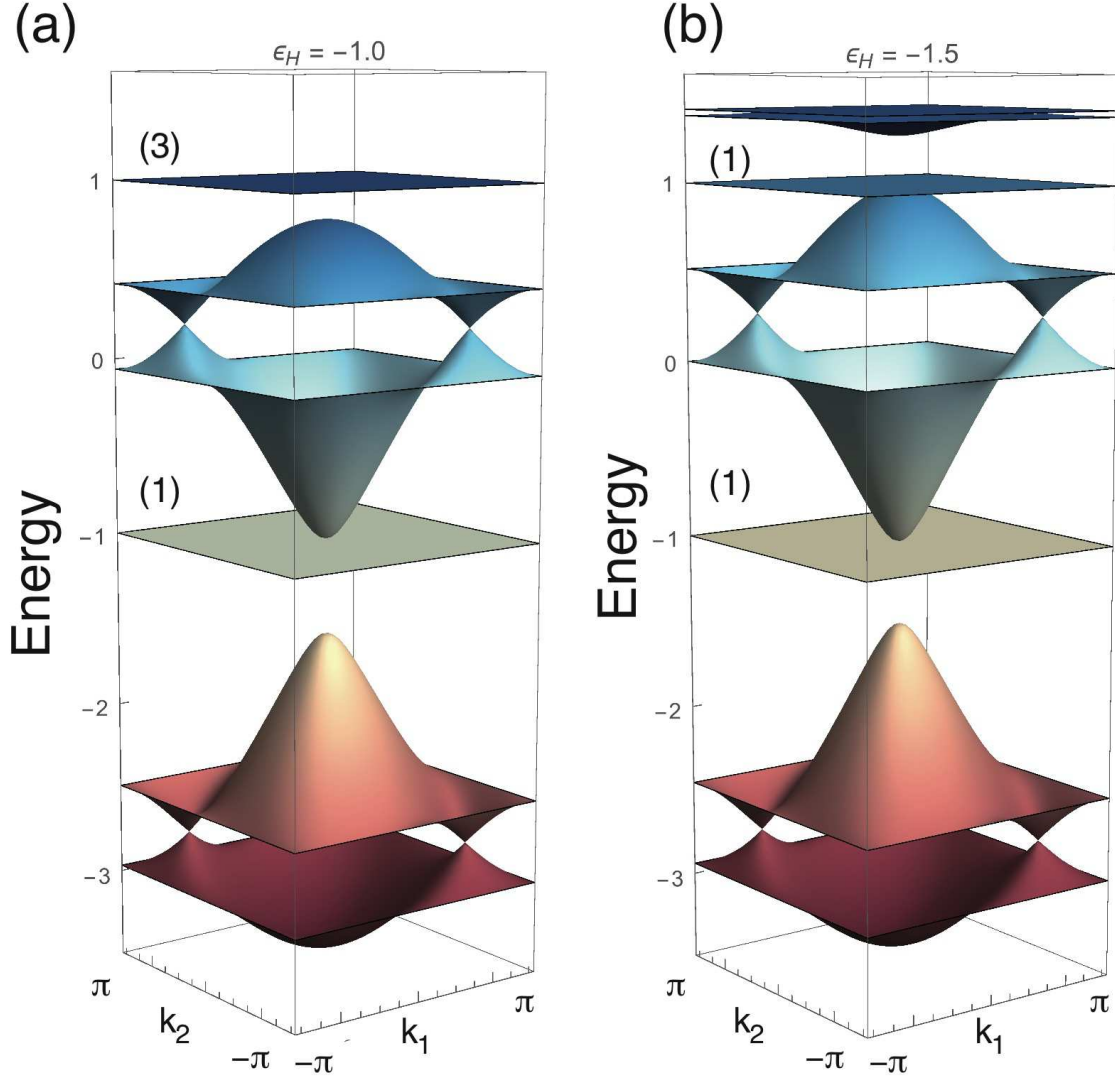


Figure 2. Band structure of the present model inspired by the WT model for silicene (with $V_1 = -0.7$ and $V_2 = -1.0$), where a region $(-\pi < k_1, k_2 < \pi)$ wider than the first Brillouin zone is displayed, and the numbers in parentheses indicate the band degeneracy. (a) The case of $\epsilon_H = V_2 = -1$, for which there are three-fold degenerate flat bands at the energy $-V_2 (= 1)$ and a non-degenerate flat band at $V_2 (= -1)$. (b) A general case with $\epsilon_H < V_2 (= -1.0)$. Here we put $\epsilon_H = 1.5V_2 = -1.5$. There are still two non-degenerate flat bands at $\pm V_2 (= \mp 1)$ touching the band that connects to the Dirac cones at S point. This is to be compared with Fig.3).

the effects can be considered by a Hamiltonian,

$$H_{\text{Silicene}}^{\epsilon_H, \cos \theta}(\mathbf{k}) = \begin{bmatrix} H_V^\theta(0) - \epsilon_H^\theta \mathcal{E} & V_2 E_4^C \\ V_2 E_4^C & H_V^\theta(\mathbf{k}) - \epsilon_H^\theta \mathcal{E} \end{bmatrix},$$

$$H_V^\theta(\mathbf{k}) = 4V_1 \psi_{\mathbf{k}}^\theta (\psi_{\mathbf{k}}^\theta)^\dagger,$$

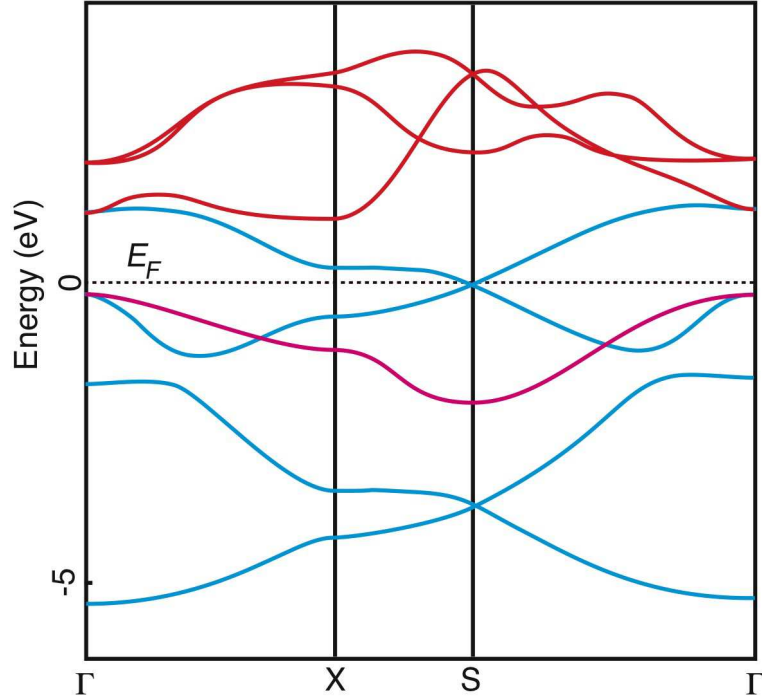


Figure 3. Band structure of silicene obtained by Takeda-Shiraishi.[4] The energy bands that can be adiabatically traced back to the flat bands are shown in red and magenta, while the pairs of bands each of which contains a massless Dirac cone are shown in blue.

$$\begin{aligned}\psi_{\mathbf{k}}^{\theta} &= \text{diag} \left(\frac{\cos \theta}{\cos \theta_0}, 1, 1, 1 \right) \psi_{\mathbf{k}}, \\ \epsilon_H^{\theta} &= \left(\frac{\cos \theta}{\cos \theta_0} \right)^2 \epsilon_H.\end{aligned}$$

This implies the Dirac cones and the flat bands we have focused are stable against the buckling. This is also regarded as an aspect of the topological stability. When the buckling becomes large enough, however, sp^2 -character of the hybridized orbitals will generate direct hoppings among the out-of-plane bonds, which is not included in the present formalism.

Conclusion

In the present paper, after introducing a generic argument for flat bands, the Weaire-Thorpe model, originally conceived for 3D silicon, is extended to 2D silicene. A surprise revealed here is that the flat bands that arise in the WT model for the hybridized sp^3 orbitals in 3D also appear, in ideal situations, in silicene, but with different degeneracies in the flat bands for an algebraic reason. In this picture, the band structure, including the flat ones, are crucially controlled by the out-of-atomic-plane orbits. We have further pointed out there are pairs of bands each of which contains a Dirac cone.

The flat bands emerging in our treatment can be theoretically interesting and

important as a multi-orbital effect[14]. Finite samples will accommodate characteristic edge states. The flat bands in the idealised model, which should become dispersive in realistic situations, will still have large density of states. If we can shift the chemical potential close to the flat bands, e.g., by chemical doping, interesting phenomena are expected. Among these are (i) structural instabilities, such as those observed experimentally, and (ii) flat-band ferromagnetism[21]. We believe that these will help for the synthesis and characterisation of silicene.

Acknowledgments

This work was supported in part by JSPS Grant Numbers 26247064(YH,HA), 25610101(YH), 25107005(HA) and 25610101 from MEXT(YH,HA).

References

- [1] Wallace, R. R., Phys. Rev. **71**, 622 (1947).
- [2] Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S.V, Grigorieva, I. V. and Firsov, A. A., Science **306**, 666 (2004).
- [3] *Physics of Graphene*, ed. H. Aoki and M. S. Dresselhaus (Springer, 2014).
- [4] Takeda, K., and Shiraishi, K, Phys. Rev. B **50**, 14916 (1994).
- [5] Lalmi, B., et al. Appl. Phys. Lett. **97**, 223109. (2012).
- [6] Vogt, P., et al., Phys. Rev. Lett. **108**, 155501 (2012).
- [7] Lin, C., -L, et al., Appl. Phys. Exp. **5**, 045802 (2012).
- [8] Weaire, D, and Thorpe, M., F., Phys. Rev. B **4**, 2508 (1971).
- [9] A related model was discussed by Dagotto E., and Fradkin E., Phys. Lett. B **172** , 383 (1986).
- [10] Hatsugai Y., and Aoki H., in *Physics of Graphene*, ed. H. Aoki and M. S. Dresselhaus (Springer, 2014), Ch.7.
- [11] Hatsugai, Y, and Maruyama, I., Europhys. Lett. **95**, 20003 (2011).
- [12] Sutherland B., Phys. Rev. B **34** , 5208 (1986).
- [13] Lieb, R., H., Phys. Rev. Lett. **62**, 1201 (1989).
- [14] Shima N., and Aoki H. [Phys. Rev. Lett. **71**, 4389 (1993)] have revealed a systematic emergence of flat band in graphene nanomesh structures, where nonzero energy flat bands are seen to exist.
- [15] Hatsugai Y., and Aoki H., New J. Phys. **15**, 035023 (2013).
- [16] Mielke, A. and Tasaki. H., Commun. Math. Phys., **158**, 341 (1993).
- [17] Katsura H., Maruyama I., Tanaka A. and Tasaki H, Europhys. Lett. **91**, 57007 (2010).
- [18] Miyahara S., Kubo K., Ono H., Shimomura Y., Furukawa N., J. Phys. Soc. Jpn. **74**, 1918 (2005).
- [19] Lomer W. M., Proc. R. Soc. London **A67**, 608 (1954).
- [20] Herring C., Phys. Rev. **52**, 365 (1937).
- [21] See, e.g., Kusakabe K., and Aoki H., Phys. Rev. Lett. **72**, 144 (1994); Okada S., Oshiyama A., Phys. Rev. Lett. **87**, 146803 (2001).